Solubility behavior of Zwitterionic polymers in aqueous solutions.

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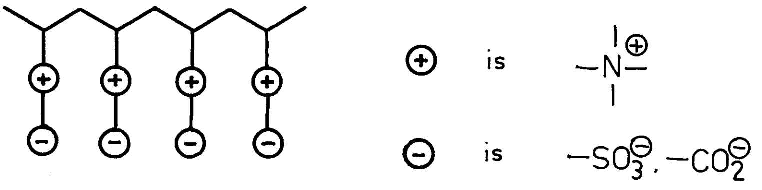
SUMMARY

This thesis describes the synthesis and solubility behavior of zwitterionic polymers. A general structure for zwitterionic polymers is depicted in scheme 1.



Scheme.1. General structure of a zwitterionic polymer.

The synthetic approach involves the preparation of the corresponding zwitterionic monomer, which is subsequently polymerized to the high molecular weight macromolecule.

In Chapter II a novel series of poly(vinylsulfobetaines) is described containing two methylene units between the opposite charges. The corresponding monomers were obtained by addition of tertiairy amines to alkenylsulfonylchlorides. The poly(vinylsulfobetaines) derived from ethenylsulfonylchloride exhibited polyzwitterionic solubility behavior in aqueous solutions (i.e. insoluble in water and solubilization upon the addition of salt). This solubility behavior has been rationalized in terms of strong intra- and intermolecular Coulombic interactions between the polymeric side groups. However, if the positive charge is effectively screened by the presence of an additional methyl substituent at the α-methylene carbon, or if the flexibility of the polymer chain is reduced by the presence of an additional methyl substituent at the imidazolium ring, the poly(vinylsulfobetaine) is soluble both in water and in salt solutions. For the latter polymers the intrinsic viscosity hardly depends on the salt concentration. This unusual solubility behavior in aqueous salt solutions, makes these types of polymers very interesting for applications in the field of enhanced oil recovery.

The synthesis and solubility behavior of a novel series of poly(vinylbetaines) is reported in chapter III. Monomeric vinylbetaines were prepared with one, two or three methylene units between the opposite charges and subsequently polymerized. In the case of one methylene unit between the opposite charges, the polymer exhibited the usual polyzwitterionic solubility

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behavior. However poly(vinylbetaines) with two or three methylene units between the opposite charges were soluble in water but upon the addition of salt further chain expansion was observed. These differences in solubility behavior were interpreted in terms of a shift in the balance between intramolecular Coulombic interactions and hydration forces, as a result of differences in the pK$_a$ of the carboxyl group. In the last two polymers a second interaction was observed, which has a profound influence on the solubility behavior. This involves hydrogen-bond formation between carboxyl and carboxylate groups, at a degree of ionization of about 0.50. These hydrogen-bond interactions give rise to precipitation or at least lowering of the [η], at well-defined salt concentrations.

For the poly(vinylbetaine) with one methylene unit between the opposite charges, a steric effect is observed in the presence of an addition methyl side group attached to the methylene unit. Now the poly(vinylbetaine) becomes soluble in water, despite the fact that the pK$_a$ is hardly influenced by the presence of the methyl side group.

In chapter IV the critical salt concentration (CSC) required to dissolve zwitterionic polymers in aqueous solution, is reported for two poly(vinylsulfobetaines) and a poly(vinylbetaine) for a variety of salts. For all three polymers the CSC's clearly depend on the nature of the anion and a Hofmeister series is observed. Larger, more polarizable anions are more effective in the solubilization of zwitterionic polymers in aqueous solution, than small, highly charged anions. In the alkali metal series hardly any influence of the size of the cation on the CSC is observed. However, changing an alkali metal cation for a tetraalkylammonium cation, results in a increase in "atmospheric binding" of anions and cations on to the polymer. Changing the alkali metal cation for a transition metal cation, results in a decrease of "atmospheric binding". These results were interpreted in terms of differences in hydration of the ions. Comparison of the CSC's for the poly(vinylsulfobetaines) with those reported in the literature, suggests the existence of strong **intra**molecular Coulombic interactions as the dominant factor in the solubility behavior of zwitterionic polymers.

A fluorescence quenching study was performed to examine the interactions of anions and cations with poly(vinylsulfobetaines) (chapter V). These experiments clearly demonstrated the interaction between the anionic quencher I$^{\ominus}$ and poly(vinylsulfobetaines). This interactions was also supported by the observation of a charge-transfer band (at 290 nm), for the poly(vinylsulfobetaine) derived form 4-vinylpyridine in an aqueous 0.05 M NaI solution. Unexpectedly, fluorescence quenching did not provide additional evidence for the interaction between soft, cations and poly(vinylsulfobetaines).

The final chapter (VI) describes an ESR spin label technique study, used to probe the micropolarity and molecular motion of a poly(vinylsulfobetaine) in aqueous solutions. It was found that the changes in the backbone segmental motion of poly(vinylsulfobetaines) in the process of solubilization in aqueous salt solution, are too small to be accurately monitored by the ESR spin label technique.

The ESR spin label technique did provide direct evidence for the conformational transition of poly(methacrylic acid) at low degree of ionization (α). At these low degrees of ionization the molecular motion of the spin label, revealed by the τ_c values, was considerably smaller as compared to that at high degrees of ionization. This is an additional indication for the presence of hydrophobic microdomains in poly(methacrylic acid) at low degrees of ionization.

Together with the "slow motion" spectrum also a "fast motion" spectrum was observed which most likely originates from those parts of the polymer which are not involved in the formation of hydrophobic microdomains. Above α=0.20 only the "fast motion" spectrum was observed, indicating a breakdown of the hydrophobic microdomains. For poly(acrylic acid), which does not form hydrophobic microdomains, no "slow motion" spectrum is observed. Further increase of the degree of ionization in both polymers, resulted in an increase of τ_c as a result of an increased stiffness of the polymer backbone. Comparison between the τ_c values for both polymers showed a significant difference in segmental motion of both polymers.

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Schema 1:

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